

UITGEGEVEN DEM

15 JUL 1937

## PATENT SPECIFICATION



Application Date: Sept. 12, 1935. No. 25368/35.

467,481

Complete Specification Left: Oct. 12, 1936.

Complete Specification Accepted: June 14, 1937.

## PROVISIONAL SPECIFICATION

## Processes of Removing Water from Aqueous Aliphatic Acids

We, KODAK LIMITED, a Company registered under the laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to processes of removing water from aqueous aliphatic acids. The usual methods of straight rectification for separating liquids, are practically impossible for dilute acetic acid because of the closeness of the vapour and liquid compositions. Consequently the use of entraining agents, also referred to as withdrawing agents, have been adopted. The following general procedure, prior to the present invention, was considered necessary, namely, excess entraining agent was employed to remove the water and produce a mixture of entraining agent and acetic acid for example, after which these constituents were separated in order to recover the acid.

According to the present invention a process of dehydrating or concentrating a lower aqueous aliphatic acid (except formic acid) is provided, comprising incorporating therewith an entraining agent consisting of an aliphatic ester and an aliphatic alcohol and removing water and agent as an azeotropic distillate therefrom. The method employed may comprise supplying to a distillation column an aqueous acid and the entraining agent and removing concentrated acid at the bottom of the column and an azeotropic mixture of water, alcohol and ester at the top of the column, the quantity of agent supplied to the column, the rate and manner of heating the column and the rate of supplying aqueous acid being so controlled that at that point in the column at which substantially the last of the water is removed the last traces of the agent will also be removed.

The agent preferably comprises an ester of the acid to be dehydrated and the corresponding alcohol,

The separated agent may be subjected to esterification before being returned to the process.

The process may be carried out in a fractionating column of known type, although it is to be noted that we have provided an apparatus for the purpose which is described hereinafter. The distilled water and entraining agent of ester and alcohol may be condensed and allowed to separate into layers. The entraining agent which forms the upper layer is generally returned to the column for re-use, while the water layer may be passed to a recovery system or discarded. In the preferred embodiment of our process, the ester alcohol entrainer passes through a cycle without serious loss and can be re-used in a continuous manner.

When using *n*-propyl acetate and *n*-propyl alcohol as entrainer we would generally prefer to use a major proportion of normal-propyl acetate and a minor proportion of normal-propyl alcohol, but the proportions of alcohol and normal-propyl acetate may be varied. In general, however, it is preferred to use an agent comprising a composition by weight of from a small amount of normal-propyl alcohol say in the neighbourhood of 3%, up to around 25%, and the balance substantially all normal-propyl acetate.

In respect to certain of the other ester-alcohol entraining agents, of which *n*-butyl acetate-*n*-butyl alcohol appears to be the most valuable and efficient, it should be noted that somewhat different proportions would be employed, for example in the case of *n*-butyl alcohol-*n*-butyl acetate the composition of the agent would comprise from about 20% to 40% *n*-butyl alcohol and the remainder mostly *n*-butyl acetate.

Propyl propionate plus propyl alcohol may be used. It is particularly advantageous for dehydrating propionic acid.

The advantage of using a mixed entrainer of ester and alcohol over certain known entrainers is explained in our application No. 15302/37.

Any of the usual types of distillation apparatus may be used in carrying out

[Price 1/-]

our process. Thus we may use the apparatus shown in our prior specification No. 383,148. However, we prefer to use the form of apparatus disclosed in the drawing forming a part of the present application, which shows a semi-diagrammatic side elevation, certain of the parts being shown in exaggerated scale and other parts being shown broken away for clarity.

When using the apparatus described in Figure 1 of our prior specification No. 383,148, and assuming *n*-propyl acetate-*n*-propyl alcohol is to be employed as entraining agent and assuming the plant to be newly constructed, it is necessary, in order to place it in operation, that the still pot 2 be charged with acid, such as, for example, concentrated acetic acid in the case of dehydrating dilute solutions of acetic acid. A supply of normal-propyl acetate-normal-propyl alcohol is placed in tank 10. Through the pipe 5 the aqueous acid is introduced slowly into the column 1 and heat applied to the still pot 2. At the same time a supply of normal-propyl acetate-normal-propyl alcohol is introduced into the column 1 through pipe 9. Upon starting the process, the lower plates of the column will contain aqueous acid.

It may be stated at this point that it is an important feature of the present invention to so control the process that the resulting dehydrated acid does not contain any of the entraining agent. In general, this may be done in the following ways: It is preferred to have just a very minute excess of water present. Should the water become too greatly in excess, a proper amount of entrainer may be added to the column, the separator, or the esterifier, to overcome this condition.

Assuming that the process is to be operated continuously, the procedure is as follows:—Upon the top plate of the column there exists a ternary azeotrope of normal-propyl acetate-normal-propyl alcohol-water. This constant boiling mixture is vaporized by the heat supplied to the column from the still pot 2 or other suitable point, and this vaporous mixture passes over through the pipe 12 into the condenser 13 where it is condensed into a liquid mixture which then passes through the pipe 14 into the separator 15.

In this separator the water, being the heavier of the liquids, settles to the bottom and passes off therefrom by means of pipe 17 leading to the sewer or, if it is desired to recover some of the agent, to a recovery system such as a flashing column. Somewhere along this return pipe 8 or at any other suitable point in the entrainer cycle, may be inserted an ester-

fying unit to control the composition of the alcohol-ester mixture.

The lower portion of the column 1 performs substantially the same function as an additional or supplemental column and will vaporize the dilute acid to meet the downwardly coming entrainer. The substantially concentrated acid refluxes into the still pot 2 where the excess accumulating is drawn off through the pipe 4 and may be conducted to storage or such use as may be desired.

If, instead of introducing the aqueous acid by means of pipe 5, it is desired to employ the supplemental still pot 19, these acid and water vapours, travelling up in the column, meet the downwardly progressing supply of normal-propyl acetate-propyl alcohol entrainer in the event this entrainer is being employed. The water combines with this entrainer and forms a ternary azeotrope which distills off and passes in a vaporous state onto the next higher plate, and so on up the column; the acid, assisting in vaporizing this azeotrope, condenses and passes down the column so that the net result, when the supplemental still pot 19 is utilized, is about the same, the difference being that the still pot prevents the column from becoming contaminated with certain impurities and the composition of the mixture upon each plate will vary slightly due to the fact that the water, in liquid or vapour form, respectively, is introduced at different positions in the column.

In the drawing accompanying the present specification, 102 represents the lower or primarily water distilling column of the unit. This column contains a plurality of bubble plate sections, usually between about 20 and 35 dependent on the capacity required and the efficiency of rectification desired.

Above, and in offset relationship to column 102, is another column designated 103, of construction similar to column 102. This column can be considered primarily as an azeotrope fractionating column.

Most of the heat required for distillation is supplied to the system by means of the calandria section 104 connected to column 103 at the column bottom 107 by conduit 106 and to the column side by conduit 108. The acid in the liquid state flows down conduit 106 into the calandria base 109.

The calandria comprises the vertically extending cylinder 104 provided with the base 109 having the valved outlet 111, for withdrawing solid residue or other materials from the calandria. The upper portion of the calandria comprises the

enlarged portion 112, provided with the cap 113 and connected to column 102 by conduit 108.

The interior of the calandria may be constructed in any suitable manner, whereby the acid liquid may be heated and vaporized. For example, a plurality of, or nests of tubes 114 arranged in any suitable boiler tube construction, such as between tube sheets 116 and 117, may be employed. The acid passes through the tubes which are surrounded by an appropriate heating medium. Usually several such sections are required and expansion means 118 may be placed between such sections.

Some of the acid liquid entering the base of the calandria is heated by passing through the several heating sections, finally vaporizing and expanding in the enlarged portion 112, whereupon it passes into column 102, through conduit 108. By virtue of heating the acid stream in this manner, a pinch effect is exerted on the liquid and a well-defined circulation down the pipe 106, up through the calandria and into the column 102 is established.

Part of the acid liquid and/or vapours, instead of circulating as just described, pass through conduits 121 and 122 into an adjacent parallel unit comprising the vertically extending cylindrical shell 123. The interior of the shell may be provided with heating means, such as for example as described with respect to calandria 104. This shell is connected at its bottom 124 with conduit 121 and at the upper part above conduit 122 with another pipe 127, which leads into the side of a small refining column designated 130.

This refining column 130 is of bubble plate construction, similar to the construction of columns 102 and 103, but on a smaller scale. The head 132 of this refining column is provided with the dephlegmator 133 which is connected by means of the valved pipe 134 with the condenser 136. In that the purified concentrated acid passes through this device, it is important that the condenser be constructed of exceptionally high grade materials, such as of the noble metals, high grade Cr-Ni steel or the like, or ceramics or glass. This condenser may be equipped with valved draw off conduits and the like 135 for removing the condensate therefrom.

A U-shaped conduit 137, which is in the nature of an overflow conduit, extends up into the lower section of the refining column and connects it with the side of calandria 104.

As will be apparent as the description proceeds, by these connections between calandria 104, unit 123 and the refining

column 130 a portion of the fully concentrated, or partially concentrated, acid (dependent on the specific process being employed) is conveniently recovered in a high state of purity in the condenser 136.

Referring now to the upper half of the water distilling column 102, there is provided a large vapour feed line 139, which branches into a plurality of vapour lines, such as 141 and 142. These branch lines lead to the head of a plurality of weak acid vaporizers 143 and 144.

These vaporizers comprise the tall cylindrical shells 146, 147 having conically shaped bottoms 148, 149, equipped with valved outlets 152, 153. The heads 154, 156 of the vaporizers are connected with the branch lines 141, 142.

These evaporators may be heated in any well known manner, either externally or internally; we prefer to employ steam coils (not shown) within the evaporators. Supplying the weak acid to be concentrated in the vapour phase from a plurality of vaporizers, as shown, has a number of advantages in a large installation. For example, the heated acid provides a source of heat at its point of introduction into the column and within the column, thereby requiring less heat to be supplied in the calandria. This better distributes the heat throughout the distillation unit. Solid impurities are kept out of the distillation columns. Also, if one vaporizer is out of use, the equipment may still be operated.

The evaporators are equipped with inlets 157, 158, for feeding in the weak acid. The weak acid may be in the form of an aqueous solution as obtained from cellulose ester manufacture, for example containing about 20—35% acid and the balance water, or the weak acid evaporated in evaporators 146, 147 might be as extract comprising acid, water and with-drawing agent.

A further preventative of impurities getting into the distillation columns is obtained by the trap provided in the vapour feed line 139, as at 145. This trap is connected by drain line 140 to the lower portion of vaporizers 146, 147 or conduits leading thereto. As indicated in the drawing, the vapour feed enters column 102 in the upper half and preferably at a point about two-thirds of the way up the lower column. In this particular setup and invention, the relationship between the vapour feed and entraining agents by-pass is of great importance.

While the invention has been described with particular reference to the two column arrangement shown, because this represents the preferred embodiment and possesses a number of advantages, such

as definition of two zones (i.e. water fractionating zone and azeotrope fractionating zone), more satisfactory construction mechanically, and other advantages, it is to be understood that the invention is not limited specifically thereto but embraces broader embodiments.

That is, the invention could be applied to a single vertical column, as for example a column comprising 30—60 plates. A suitable vertical column is shown in Fig. 1 of our prior specification No. 383,143. Or, instead of employing two columns, three or more might be employed. The process being operated to maintain the separate zones therein in accordance with the present disclosure.

Referring again to the preferred embodiment, column 102 is provided with the horizontally extending vapour outlet 161, through which the vapours fractionated in column 102 may be conducted to the next and upper column 103. The liquid flowing down column 103 is conducted by a U-shaped conduit 162 into a plate section in the lower column 102.

The upper column 103 is provided with a vapour outlet conduit 163 for conducting off the vapours fractionated in this azeotrope column. These vapours are condensed in condenser 164, after which the condensate is led through pipe 166 to the decanter 167. Pipe 166 is provided with the expansion loop 168 and the valved branch conduit 169. This branch conduit may be employed to withdraw or by-pass materials from the system.

The decanter 167 comprises a tank having the sidewalls 171, a bottom 172 and top 173, the condensate pipe 166 being connected to the top. The decanter assembly includes two over-flow basins, namely the inside overflow 174 and the outside overflow 176. The positioning of these overflows and associated parts will be governed by whether the withdrawing agent being employed is heavier or lighter than water. Assuming the apparatus set-up is to employ an ester-alcohol agent with a density less than water, so that it will form the top layer in the decanter, then the arrangement of overflow is as shown in the accompanying drawing. That is, the inside overflow 174 is positioned in the upper part of decanter 167. To obtain easy and proper flow the overflow may be equipped with an elliptical-shaped mouth. The overflow is connected by means of conduit 177, having the trap 178, to column 103 at about the top plate.

Branching from conduit 177 is the pipe 179, which leads to the sight glass and meter 181. A valve is provided at 182 to assist in controlling the flow of withdraw-

ing agent in this branched line. Another pipe 183 having a liquid trap 184 connects the sight glass meter 181 with the lower column 102, preferably at the head of this column.

As the description proceeds it will be apparent that the arrangement and functioning of this branch line 179, 181, 183 is of great importance in operating in accordance with the present invention to obtain highly efficient results. Referring again to decanter 167, it will be noted that the outside overflow 176 is positioned on about the same level as the inside overflow. In the case under consideration, where the water layer is the lower one, the outside overflow basin is connected to the bottom of the decanter by pipe 186, through which, when the decanter is filled to the proper level the decanted liquid will cause the water to rise into overflow basin 176. The interior of this basin contains a second adjustable shallow overflow mouth 187, whereby the aqueous layer can be caused to flow smoothly out of the overflow 176 and through either conduit 188 or 189, whichever is preferred, the pipe 189 providing means of refluxing water if desired. The conduit 188 may be connected (by valved pipe 190) to the flush column 191, of usual construction which is provided with a vapour outlet 192 and condenser 193 wherein the agent flushed over is condensed and returned to the decanter, conduit 177, or such other point as is satisfactory. The heated water coming from the flush column may be passed through a heat exchanger to recover the heat therefrom before discharge to the sewer.

The exact amount of decanted agent to by-pass is governed by specific details, however, when employing an alcohol-containing agent of the type described, generally by-passing between 3—30% of the decanted entrainer will be satisfactory.

The amount by-passed can be controlled and observed by means of valve 182, sight glass and meter 181 and the size of pipes 179, 183.

The production of concentrated acid by the new procedure when compared with the prior art may appear to involve operation with an insufficiently and improperly charged azeotropic distillation unit. However, that is not the case. The unit operates so that most of the water present is removed from the acid in the lower part of the distillation unit by simple fractionation. While this fractionated water will carry with it substantial quantities of acid, as it passes up through the bubble plates some separation takes place, but in any event, material losses of acid do not

occur because the water and acid contact the azeotrope-forming entrainer in the upper part of the unit with the result that the water is separated from the acid being carried along the acid returning to the lower part of the unit.

The process may also be carried out in the apparatus shown in Fig. 1 of our application No. 15302/37 by ensuring that column 41 contains an excess of water. The partially dehydrated acid in vessel 44 is conducted through valved pipe 54 to an intermediate portion of an auxiliary fractionating column 55 where the quantity of entrainer is carefully controlled in a manner, as previously described, to yield anhydrous acid uncontaminated with agent.

There are a number of advantages

derived from this two-step concentration such as for example: Dilute acid of various strengths and from various sources may be readily concentrated, in the first step operating with an excess water, to produce an acid of uniform strength say around 90%. This uniform partially concentrated acid is then completely dehydrated under carefully controlled conditions. These features are of importance to users of large quantities of acid from various sources since it provides a method in which expert control is required in removing only a small quantity of water.

Dated this 9th day of September, 1935.

W. P. THOMPSON & Co.,  
12, Church Street, Liverpool, 1,  
Chartered Patent Agents.

## COMPLETE SPECIFICATION

### Processes of Removing Water from Aqueous Aliphatic Acids

We, KODAK LIMITED, a Company registered under the laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to processes of removing water from aqueous aliphatic acids. The invention is concerned with processes of the type in which the water in the vapours of an aqueous acid is carried off, with the aid of an entraining agent whose vapours form an azeotropic mixture with water vapour, from a rectifying column into the lower part of which vapours of the acid are distilled while the entraining agent is supplied at the upper part and the aqueous acid at an intermediate point. This type of process is to be distinguished therefore from a process in which the entraining agent is supplied in admixture with the acid to be concentrated (see specification No. 356,787). The present invention is applicable to the treatment of mixtures of one or more of the aliphatic acids (other than formic acid) with water in any proportion or to the treatment of aqueous liquors containing one or more of these acids. The dehydration of aqueous acetic acid is, however, of particular importance. Processes of the type

described are generally employed for this purpose, because the closeness of the vapour and liquid compositions renders the usual methods of straight rectification practically impossible for dilute acetic acid.

It has been customary in practice, and was thought necessary, in processes of this type, to feed the entraining agent and dilute acid in at such rates that the entraining agent was present in excess at all points in the system at which distillation occurs or at least at the point where the last vaporisation of azeotropic mixture occurs. This resulted in producing a mixture of entraining agent and acetic acid, after which these constituents were separated in order to recover the acid. When the boiling point of the entraining agent is near that of the acid it is extremely difficult to separate the acid and the entraining agent.

The present invention relates to a process of the type described for dehydrating or concentrating a lower aqueous aliphatic acid (except formic acid) or a mixture of such acids in which there is used an entrainer consisting of an ether, ketone, ester or ester-alcohol mixture which boils (or whose components boil) at a temperature between 25° below and 30° above the boiling point of the acid and which forms with the water an azeotropic mixture boiling below 100° C., and in which the quantity of agent supplied, the rate and manner of heating and the rate of supplying aqueous acid are so controlled that the lower part of the rectifying apparatus is maintained free from entraining agent and serves to rectify aqueous acid and to

reflux a substantially more concentrated acid. The difficult step of separating acid and entraining agent is thus avoided.

The sufficiency of the entraining agent 5 may be determined by employing such an amount that it does not appear below the inlet for the aqueous acid, which, as already stated, is below the inlet for entraining agent, a point of great importance in the present invention where the entraining agent boils at a temperature within the limits stated.

The rectifying apparatus may be in two parts to the lower of which the aqueous acid is fed the concentrated or dehydrated acid being withdrawn from the bottom and aqueous acid vapour being withdrawn from the top and passed to the upper part, into the upper end of which upper part 20 entraining agent is introduced and from the lower end of which rectified acid is withdrawn and returned to the top of the lower part.

In carrying out this form of the invention, we may use the two column arrangement shown in the drawing accompanying the provisional specification or that shown in Figure 2 of our prior patent No. 383,148. A two column arrangement in 30 effect provides a division of the rectifying apparatus into two parts and is to be preferred as it possesses a number of advantages, such as definition of two zones (i.e. water fractionating zone and azeotrope 35, fractionating zone), and more satisfactory construction mechanically. It is to be understood, however, that the invention could also be practised with the aid of a single vertical column such as that 40 shown in Figure 1 of our prior patent No. 383,148, as for example, a column comprising 30—60 plates. Or, instead of employing two columns, three or more might be employed; the process being 45 operated to maintain the separate zones therein in accordance with the present invention, and the columns whether two, three or more forming a combined unit.

The entraining agent which distils off 50 with the water may be recovered and re-used in a continuous manner as is customary in processes of this kind and indeed the process as a whole is particularly adapted for continuous operation.

55 The entraining agent preferably comprises an aliphatic alcohol and an ester of the acid or of at least one of the acids to be concentrated or dehydrated. Preferably the alcohol corresponds to the ester 60 or esters. An alcohol containing five carbon atoms, i.e. amyl alcohol or one of its isomers, is particularly suitable when used in conjunction with the ester of the alcohol with the acid to be concentrated.

65 The use of such an entraining agent for

the concentration or dehydration of aqueous aliphatic acids under specific conditions in which esterification is avoided is claimed in our co-pending application No. 15302/37.

Among other entraining agents, not being alcohol-ester mixtures, which can be employed in carrying out the present invention may be mentioned the following substances to which are appended, for convenience, their normal boiling points:—

Allyl acetate 105° C.; dichloromethyl ether 106°; butyl formate 107°; ethyl iso amyl ether 112°; iso butyl acetate 118°; allyl iso amyl ether 120°; ethyl amyl ether 120°; chloroacetone 121°; dibutyl ether (sec) 121°; ethyl butyrate 121°; dibutyl ether (iso) 123°; propyl propionate 123°; iso-amyl formate 124°; ethyl propyl ketone 124°; butyl acetate 127°; methyl butyl ketone 127°; allyl acetone 129°; crotonyl acetate 129°; mesityl oxide 129°; amyl formate 130°; butyl propionate 137°; dibutyl ether 141°; iso amyl acetate 142°; propyl butyrate 143°; dipropyl ketone 144°; amyl acetate 148°.

Certain of these liquids are more efficient from the standpoint of heat costs, others may be more efficient from the standpoint of ease of separation of substantially pure water at the still head. In some cases, as, for example, with butyl ether, some acid may, under some conditions, be found in the water at the still head unless an extremely long column is used. This is not always undesirable, but when acid free water is wanted, choice will be made of another material, such as allyl acetate to give this result. Mixtures of some of these liquids may be used.

The final rectification of the acid by straight rectification without entrainer, renders it possible, as will have already appeared, to use in the process entrainers, in the concentration of acetic acid by continuous operation, boiling at temperatures above the boiling point of the acid.

The process of concentration or dehydration according to the invention may be applied to acids of any concentration. Thus the process is very effective for the concentration of 30% acetic acid but 5% and 85% acetic acid may also be concentrated. The process may also be used for propionic and butyric acids, or mixture of these with acetic acid, especially such mixtures in which acetic acid predominates.

In the case where a single column is employed as the dehydrating apparatus the lower part serves for simple rectification and the aqueous acid is fed in above this lower part.

Any of the usual types of distillation

70

75

80

85

90

95

100

105

110

115

120

125

130

apparatus may be used in carrying out our process. In particular, as already stated, we may use the apparatus illustrated and described in our prior patent No. 383,148.

Where a single column still is used, one of approximately 52 plates construction has been found to be suitable, although it is to be understood that other size columns may be used, and, in fact, one containing 33 plates can be successfully used. The longer column is preferred, since it gives more efficient rectification. However, we prefer to use the form of apparatus illustrated in the drawing accompanying the provisional application. This drawing shows a semi-diagrammatic side elevation of one form of apparatus in which our process may be carried out, certain of the parts being shown in exaggerated scale.

In the drawing 102 represents the lower or water distilling column of the unit. This column contains a plurality of bubble plate sections, usually between about 20 and 35 dependent on the capacity required and the efficiency of rectification desired.

Above, and in offset relationship to column 102, is another column designated 103, of construction similar to column 102, this column can be considered primarily as an azeotrope fractionating column.

Most of the heat required for distillation is supplied to the system by means of the calandria section 104 connected to column 102 at the column bottom 107 by conduit 106 and to the column side by conduit 108. The acid in the liquid state flows down conduit 106 into the calandria base 109.

The calandria comprises the vertically extending cylinder 104 provided with the base 109 having the valved outlet 111, for withdrawing solid residue or other materials from the calandria. The upper portion of the calandria comprises the enlarged portion 112, provided with the cap 113 and connected to column 102 by conduit 108.

The interior of the calandria may be constructed in any suitable manner, whereby the acid liquid may be heated and vaporized. For example, a plurality of, or nests of, tubes 114 arranged in any suitable boiler tube construction, such as between tube sheets 116 and 117, may be employed. The acid passes through the tubes which are surrounded by an appropriate heating medium. Usually several such sections are required and expansion means 118 may be placed between such sections.

Some of the acid liquid entering the base of the calandria is heated by passing

through the several heating sections, finally vaporizing and expanding in the enlarged portion 112, whereupon it passes into column 102, through conduit 108. By virtue of heating the acid stream in this manner, a pinch effect is exerted on the liquid and a well-defined circulation down the pipe 106, up through the calandria and into the column 102 is established.

Part of the acid liquid and/or vapours, instead of circulating as just described, pass through conduits 121 and 122 into an adjacent parallel unit comprising the vertically extending cylindrical shell 123. The interior of the shell may be provided with heating means, such as for example as described with respect to calandria 104. This shell is connected at its bottom 124 with conduit 121 and at the upper part above conduit 122 with another pipe 126, which leads into the side of a small refining column designated 130.

This refining column 130 is of bubble plate construction, similar to the construction of columns 102 and 103, but on a smaller scale. The head 132 of this refining column is provided with the dephlegmator 133 which is connected by means of the valved pipe 134 with the condenser 136. In that the purified concentrated acid passes through this device, it is important that the condenser be constructed of exceptionally high grade materials, such as of the noble metals, high grade Cr-Ni steel or the like, or ceramics or glass. This condenser may be equipped with valved draw off conduits and the like 135 for removing the condensate therefrom.

A U-shaped conduit 137, which is in the nature of an overflow conduit, extends up into the lower section of the refining column and connects it with the side of calandria 104.

As will be apparent as the description proceeds, by these connections between calandria 104, unit 123 and the refining column 130 a portion of the fully concentrated, or partially concentrated, acid (dependent on the specific process being employed) is conveniently recovered in a high state of purity in the condenser 136.

Referring now to the upper half of the water distilling column 102, there is provided a large vapour feed line 139, which branches into a plurality of vapour lines, such as 141 and 142. These branch lines lead to the head of a plurality of weak acid vaporizers 143 and 144.

These vaporizers comprise the tall cylindrical shells 146, 147 having conically shaped bottoms 148, 149, equipped with valved outlets 152, 153. The heads 154, 156 of the vaporizers are connected with the branch lines 141, 142.



These evaporators may be heated in any well known manner, either externally or internally; we prefer to employ steam coils (not shown) within the evaporators.

5 Supplying the weak acid to be concentrated in the vapour phase from a plurality of vaporizers, as shown, has a number of advantages in a large installation. For example, the heated acid 10 provides a source of heat at its point of introduction into the column and within the column, thereby requiring less heat to be supplied in the calandria. This better distributes the heat throughout the distillation unit. Solid impurities are 15 kept out of the distillation columns. Also, if one vaporizer is out of use, the equipment may still be operated.

The evaporators are equipped with 20 inlets 157, 158, for feeding in the weak acid. The weak acid may be in the form of an aqueous solution as obtained from cellulose ester manufacture, for example, containing about 20—35% acid and the 25 balance water, or the weak acid evaporated in evaporators 146, 147 might be an extract comprising acid, water and withdrawing agent.

A further preventative of impurities 30 getting into the distillation columns is obtained by the trap provided in the vapour feed line 139, as at 145. This trap is connected by drain 140 to the lower portion of vaporizers 146, 147 or 35 conduits leading thereto. As indicated in the drawing, the vapour feed enters column 102 in the upper half and preferably at a point about two-thirds of the way up the lower column. In this particular 40 setup and invention, the relationship between the vapour feed and withdrawing agents by-pass is of great importance.

Column 102 is provided with the 45 horizontally extending vapour outlet 161, through which the vapours fractionated in column 102 may be conducted to the next and upper column 103. The liquid flowing down column 103 is conducted by 50 a U-shaped conduit 162 into a plate section in the lower column 102.

The upper column 103 is provided with a vapour outlet conduit 163 for conducting off the vapours fractionated in this 55 azeotrope column. These vapours are condensed in condenser 164, after which the condensate is led through pipe 166 to the decanter 167. Pipe 166 is provided with the expansion loop 168 and the valved 60 branch conduit 169. This branch conduit may be employed to withdraw or by-pass materials from the system.

The decanter 167 comprises a tank having the sidewalls 171, a bottom 172 65 and top 173, the condensate pipe 166 being

connected to the top. The decanter assembly includes two over-flow basins, namely, the inside overflow 174 and the outside overflow 176. The positioning of these overflows and associated parts will 70 be governed by whether the withdrawing agent being employed is heavier or lighter than water. Assuming the apparatus set-up is to employ an ester-alcohol agent with a density less than water, so that it 75 will form the top layer in the decanter, then the arrangement of overflow is as shown. That is, the inside overflow 174 is positioned in the upper part of decanter 167. To obtain easy and proper flow the 80 overflow may be equipped with an elliptical-shaped mouth. The overflow is connected by means of conduit 177, having the trap 178, to column 103 at about the top plate. 85

Branching from conduit 177 is the pipe 179, which leads to the sight glass and meter 181. A valve is provided at 182 to assist in controlling the flow of withdrawing agent in this branched line. 90 Another pipe 183 having a liquid trap 184 connects the sight glass meter 181 with the lower column 102, preferably at the head of this column.

As the description proceeds it will be 95 apparent that the arrangement and functioning of this branch line 179, 181, 183 is of great importance in operating in accordance with the present invention to obtain highly efficient results. Referring 100 again to decanter 167, it will be noted that the outside overflow 176 is positioned on about the same level as the inside overflow. In the case under consideration, where the water layer is the lower one, 105 the outside overflow basin is connected to the bottom of the decanter by pipe 186, through which, when the decanter is filled to the proper level the decanted liquid will cause the water to rise into overflow 110 basin 176. The interior of this basin contains a second adjustable shallow overflow mouth 187, whereby the aqueous layer can be caused to flow smoothly out of the over- 115 flow 176 and through either conduit 188 or 189, whichever is preferred, the pipe 189 providing means of refluxing water if desired. The conduit 188 may be connected (by valved pipe 190) to the flash 120 column 191, of usual construction which is provided with a vapour outlet 192 and condenser 193 wherein the agent flashed over is condensed and returned to the decanter, conduit 177, or such other point 125 as is satisfactory. The heated water coming from the flash column may be passed through a heat exchanger to recover the heat therefrom before discharge to the sewer.

The exact amount of decanted agent to 130



by-pass is governed by specific details, however, when employing an alcohol-containing agent of the type described, generally by-passing between 3—30% of the decanted entrainer will be satisfactory.

The amount by-passed can be controlled and observed by means of valve 182, sight glass and meter 181 and the size of pipes 179, 183.

The production of concentrated acid by the new procedure when compared with the prior art may appear to involve operation with an insufficiently and improperly charged azeotropic distillation unit. However, that is not the case. The unit operates so that most of the water present is removed from the acid in the lower part of the distillation unit by simple fractionation. While this fractionated water will carry with it substantial quantities of acid, as it passes up through the bubble plates some separation takes place, but in any event, material losses of acid do not occur because the water and acid contact the azeotrope-forming entrainer in the upper part of the unit with the result that the water is separated from the acid being carried along the acid returning to the lower part of the unit.

The process when conducted in the apparatus shown in Figure 2 of our prior patent No. 383,148 is operated so that column 41 contains an excess of water. The partially dehydrated acid in vessel 44 is conducted through valved pipe 54 to an intermediate portion of the auxiliary fractionating column 55 where the quantity of entrainer is carefully controlled in a manner, as previously described to yield anhydrous acid uncontaminated with agent.

There are a number of advantages derived from this two-step concentration such as, for example: Dilute acid of various strengths and from various sources may be readily concentrated, in the first step operating with an excess water, to produce an acid of uniform strength say around 90%. This uniform partially concentrated acid is then completely dehydrated under carefully controlled conditions. These features are of importance to users of large quantities of acid from various sources since it provides a method in which expert control is required in removing only a small quantity of water.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by our foreign correspondents, we declare that what we claim is:—

1. A process of concentrating or dehydrating a lower aqueous aliphatic acid (except formic acid) or a mixture of such acids of the type described in which an entraining agent is employed consisting of an ether, ketone, ester, or ester alcohol mixture having a boiling point between 25° below and 30° above the boiling point of the acid to be concentrated or dehydrated and which forms with the water an azeotropic mixture boiling below 100° C. and in which the quantity of agent supplied, the rate and manner of heating the column and the rate of supplying aqueous acid are so controlled that the lower part of the rectifying column is maintained free from entraining agent and serves to rectify aqueous acid and to reflux a substantially more concentrated acid.

2. The process as claimed in Claim 1, in which the rectifying column is in two parts to the lower of which the aqueous acid is fed, the concentrated or dehydrated acid being withdrawn from the bottom and aqueous acid vapour being withdrawn from the top and passes to lower end of the upper part, into the upper end of which upper part entraining agent is introduced and from the lower end of which rectified acid is withdrawn and returned to the top of the lower part.

3. The process as claimed in Claims 1 or 2 in which heat is supplied to the rectifying column by feeding vapours of the concentrated or dehydrated acid to the lower part below the feed of aqueous acid.

4. The process as claimed in any of the preceding claims in which the entraining agent is supplied to the rectifying apparatus in an amount insufficient to permit it to be present in the apparatus below the inlet for the aqueous acid.

5. The process as claimed in any of the preceding claims in which the entraining agent distilled off with the water as an azeotropic mixture is recovered and re-used in a continuous manner.

6. The process as claimed in any of the preceding claims in which aqueous acid is continuously supplied and continuously vapourised and rectified, entraining agent is continuously supplied and an azeotropic vapour consisting of entraining agent and water is continuously removed.

7. The process as claimed in any of the preceding claims in which the entraining agent comprises a mixture of an aliphatic alcohol and an ester of the acid or of at least one of the acids to be concentrated or dehydrated.

8. The process as claimed in Claim 7 in which the alcohol in the entraining agent corresponds to the ester or esters therein.

Dated this 10th day of October, 1936.

W. P. THOMPSON & Co.,  
12, Church Street, Liverpool,  
Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1937.

[This Drawing is a reproduction of the Original on a reduced scale.]

